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**10/575722** F10400609 IAP15 Rec'd PCT/PTO 13 APR 2006

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WO 96/05054 describes a recyclable paper of the same type as the one previously described, except for the fact that the second layer consists advantageously of a styrene-butadiene copolymer used in maximum proportions of 90 % by dry weight of the layer.

DE-A-4445193 describes a paper comprising a support coated with a composite three-layered gas barrier. The three-layered composite is formed of a metal layer situated in a sandwich structure between two layers of film-forming polymers, the polymer being heat sealable. The coating must thus take place in three separate steps, the first film-forming polymer, the metal layer and the second film-forming polymer respectively.

The applicant has noticed that the use of a mixture of acrylic polymers as an emulsion, having a total acid number of between 30 and 65, and a wax concentration less than 5 %, reduced strongly the permeability to water vapour. Such a product corresponds e.g. to a product sold by the MICHELMAN company under the name "MR130".

This product can be used for manufacturing cold or hot sealable papers, but also twistable papers for confectionery.

Consequently and according to a first characteristic, the invention concerns a cold sealable barrier paper consisting of an actual support paper printed on the face side thereof, and having a sealable layer on the whole or on one part of the *reverse* side thereof. This paper is characterized in that it further has, on the *face* side thereof, a water vapour barrier layer comprising a mixture of acrylic polymers as an emulsion, the total acid number\_of which is between 30 and 65, the mixture comprising less than 5 % of wax by weight.

In the rest of the description and in the claims, the expressions are defined as follows:

- "total acid number" denotes the milligrams of potassium hydroxide needed for neutralizing the acidity of one gram of polymer in normalized conditions,
- "actual support paper" denotes a coated calendered (cellulose + pigment layer composed of mineral pigments and of a latex-type binder) or uncoated calendered (consisting of only cellulose) support paper, the

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one previously described, except for the fact that the second layer consists advantageously of a styrene-butadiene copolymer used in maximum proportions of 90 % by dry weight of the layer.

DE-A-4445193 describes a paper comprising a support coated with a composite three-layered gas barrier. The three-layered composite is formed of a metal layer situated in a sandwich structure between two layers of film-forming polymers, the polymer being heat sealable. The coating must thus take place in three separate steps, the first film-forming polymer, the metal layer and the second film-forming polymer respectively.

US-A-5 429 294 discusses a manufacture of folding or corrugated boxes. The box material includes a water barrier, and the barrier property is totally dependent on the amount of wax in the coating. The document teaches that the amount of wax needed is 4 to 12 pounds per one thousand square feet (equals to 20 to 57  $g/m^2$ ).

FR-A-2 745 553 discusses a barrier paper structure, where, on the one hand, that the functioning of the barrier layer is totally dependent on the presence of a metal layer, and, on the other hand, that the metal layer requires a varnish layer on both sides thereof.

The applicant has noticed that the use of a mixture of acrylic polymers as an emulsion, having a total acid number of between 30 and 65, and a wax concentration less than 5 %, reduced strongly the permeability to water vapour. Such a product corresponds e.g. to a product sold by the MICHELMAN company under the name "MR130".

This product can be used for manufacturing cold or hot sealable papers, but also twistable papers for confectionery.

Consequently and according to a first characteristic, the invention concerns a cold sealable barrier paper consisting of an actual support paper printed on the face side thereof, and having a sealable layer on the whole or on one part of the face side thereof. This paper is characterized in that it further has, on the reverse side thereof, a water vapour barrier layer comprising a mixture of acrylic polymers as an emulsion, the total acid number of which is

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mass of which is between 25 and 110 g/m<sup>2</sup>, advantageously between 25 and 60 g/m<sup>2</sup>.

Likewise, the printing corresponds to one or more ink layers, the layers being deposited by any technique, such as heliogravure or flexogravure printing, known by a person skilled in the art.

Moreover, the expression "cold sealable layer" denotes a layer prepared from natural or synthetic latex; these formulations are denoted by the term "cold seal" by those skilled in the art, the layer being applied in an amount of 2 - 5 g/m<sup>2</sup>.

The wax present in the acrylic polymer mixture is notably paraffin.

As already mentioned, the water vapour barrier layer consists of a mixture of acrylic polymers as an emulsion, the total acid number of which is between 30 and 65, the mixture representing advantageously 100 % by dry weight of the layer. Advantageously, the mixture of polymers contains from 2 to 10 % by weight of resin and less than 5% of wax by weight. Preferably, the mixture of acrylic polymers is a mixture of styrene-acrylic polymers.

The cold sealable paper of the invention can appear in several forms.

In a first embodiment, the water vapour layer is positioned directly on the printing, which itself is directly in contact with the actual paper.

In practice, this layer can be applied at one go, respectively in an amount of  $2 - 10 \text{ g/m}^2$  as humid matter or of  $1 - 5 \text{ g/m}^2$  as dry matter, by any technique known by a person skilled in the art, such as especially but in a non limitative manner, heliogravure or reverse roll.

The sealable layer is, in turn, applied directly on the whole or on one part of the reverse side of the actual paper, in an amount of for example 1 – 5 mg/m<sup>2</sup> as dry matter, especially by the helio coating technique.

Moreover, the applicant has noticed that, completely surprisingly, the polymer constitutive of the water vapour barrier layer had anti-adherent properties, whereby the presence of a supplemental anti-adherent layer on the water vapour barrier layer becomes unnecessary.

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aroma barrier layer is inserted, which is of the same type as previously described in case of the cold sealable paper.

In order to protect the oxygen barrier layer and to enhance the water vapour layer without affecting the sealability, the paper has additionally a second water vapour barrier layer deposited directly on the printing.

Finally, the specific water vapour barrier layer of the invention can also be applied to confectionery papers, i.e. for twistable papers.

In this case, the paper for confectionery intended to be twistable consists of an actual twistable support paper, the face of which is printed or printable. This paper is characterized in that a water vapour barrier layer, comprising a mixture of acrylic polymers as an emulsion, the total acid number of which is between 30 and 65, the mixture having less than 5 % of wax by weight, is deposited on the printing.

In an advanced embodiment, the twistable paper has oxygen and aroma barrier properties. In this case, between the water vapour barrier and the printing there is inserted an oxygen and aroma barrier layer of the previously described type, i.e. a layer comprising an ethylene/vinyl alcohol (EVOH) copolymer or polyvinyl alcohol (PVA) polymer, the mass of which is between 3 and 4 g/m<sup>2</sup>.

In the same way as previously, in an advantageous embodiment, the mixture of acrylic polymers as an emulsion contained in the water vapour barrier layer further contains from 2 to 10 % of resin and represents 100 % by dry weight of the layer. In a preferred embodiment, the mixture of acrylic polymers is a mixture of styrene acrylic polymers. Accordingly, the wax is notably paraffin.

In an advantageous embodiment, the reverse side of the support paper is provided with a paraffin layer, the mass of which is between 2 and 6 g/m<sup>2</sup>.

The invention and the advantages, which stem therefrom will become more apparent from the following illustrative examples supported by the appended figures.

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In an advanced embodiment, the twistable paper has oxygen and aroma barrier properties. In this case, between the water vapour barrier and the printing there is inserted an oxygen and aroma barrier layer of the previously described type, i.e. a layer comprising an ethylene/vinyl alcohol (EVOH) copolymer or polyvinyl alcohol (PVA) polymer, the mass of which is between 3 and 4 g/m<sup>2</sup>.

In the same way as previously, in an advantageous embodiment, the mixture of acrylic polymers as an emulsion contained in the water vapour barrier layer further contains from 2 to 10 % of resin and represents 100 % by dry weight of the layer. In a preferred embodiment, the mixture of acrylic polymers is a mixture of styrene acrylic polymers. Accordingly, the wax is notably paraffin.

In an advantageous embodiment, the reverse side of the support paper is provided with a paraffin layer, the mass of which is between 2 and 6

The above-discussed invention makes it possible to use new types of paper-based materials for packaging food, coffee or washing powder, for example. Earlier either plastics or specifically designed paper-based materials have been used. For both environmental and recyclability reasons both plastic materials and papers having metal foils or layers and/or heavy wax content have

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been less desirable, as the plastics and/or metal foils do not degrade in itself in the nature, and the waxes, in higher amounts, cause problems in case the materials are recycled.

Now the present invention discusses a novel paper-based material for the above-discussed types of packaging, the material being free of metal foils or layers, and including such a low amount of wax that the presence of wax does not take away the recyclability of the material.

The invention and the advantages, which stem therefrom, will become more apparent from the following illustrative examples supported by the appended figures.

Figure 1 illustrates a first embodiment of a cold sealable water vapour barrier paper according to the invention.

Figure 2 (2A, 2B) illustrates an advanced embodiment of the figure 1, in which the presence of at least one oxygen and aroma barrier layer is provided.

Figure 3 illustrates a heat sealable water vapour barrier paper according to the invention.

Figure 4 illustrates an advanced embodiment of the figure 3, in which at least one oxygen and aroma barrier layer is provided.

Figure 5 illustrates an advanced embodiment of the figure 4, in which a second water vapour barrier layer is provided.

Figure 6 illustrates a water vapour barrier paper for confectionery according to the invention.

Figure 7 illustrates a second embodiment of a water vapour barrier paper for confectionery according to the invention.

Figure 8 illustrates advanced embodiments of the figure 6, in which at least one oxygen and aroma barrier is provided.

The different examples hereinafter describe the assembly of structures of cold, heat sealable papers or of twistable papers covered by the

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## **EXAMPLE 7: Twistable paper**

Example 7 corresponds to an advanced embodiment of the example6 and is represented in the figure 7.

In this illustrative example, the reverse side of the support paper is coated with paraffin (7), the mass of which is  $3 \text{ g/m}^2$ .

## **EXAMPLE 8: Twistable paper**

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Example 8 corresponds to an advanced embodiment of the example 6 insofar as the structure further contains at least one oxygen and aroma barrier layer 5, this layer being positioned e.g. between the water vapour barrier layer and the printing layer (figure 8).

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## **EXAMPLE 9:**

An example of the water vapour barrier for the structure, object of the example 3.

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PVE = 20 g/m²/day, 38°C, 90 % relative humidity.

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## **CLAIMS**

1. Cold sealable barrier paper consisting of an actual support paper (1) printed on the face side thereof and having a sealable layer (3) on the whole or on one part of the reverse side thereof, **characterized** in that it further consists, on the face side thereof, of a water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65.

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- 2. Cold sealable barrier paper consisting of an actual support paper (1) printed on the face side thereof and having a sealable layer (3) on the whole or on one part of the reverse side thereof, characterized in that it further consists, on the face side thereof, of a water vapour barrier layer (4) consisting of a mixture of acrylic polymers and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, and of at least one oxygen aroma barrier layer (5) between the printing (2) and the water vapor barrier layer (4), or between the actual support paper and the sealable layer, the oxygen aroma barrier layer (5) consisting of ethylene/vinyl alcohol (EVOH) copolymer or polyvinyl alcohol (PVA) polymer, the mass of which is between 3 and 4 g/m<sup>2</sup>.
- 3. Cold sealable barrier paper consisting of an actual support paper (1) printed on the face side thereof and having a sealable layer (3) on the whole or on one part of the reverse side thereof, **characterized** in that it further consists, on the face side thereof, of a water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, and the mixture comprising less than 5% of wax by weight, and of at least one oxygen aroma barrier layer (5) between the printing (2) and the water vapor barrier layer (4), or between the support paper (1) and the sealable layer (3), the oxygen aroma barrier layer (5) consisting of ethylene/vinyl

alcohol (EVOH) copolymer or polyvinyl alcohol (PVA) polymer as a mixture with other polymers or as a mixture with mineral fillers, the EVOH or PVA representing at least 50 % by weight of the layer.

- 5 4. Cold sealable barrier paper according to any of claims 1 to 3, characterized in that the water vapour barrier layer is positioned directly in contact with the printing and has a mass of between 2 and 10 g/m² as humid matter.
- 5. Cold sealable barrier paper according to any of claims 1 to 4, characterized in that the sealable layer is positioned directly in contact with the whole or one part of the reverse side of the actual paper.
- Cold sealable barrier paper according to any of claims 1 to 5,
  characterized in that the mixture of acrylic polymers as an emulsion is a mixture of styrene acrylic polymers.
- Cold sealable barrier paper according to any of claims 1 to 6,
  characterized in that the mixture of acrylic polymers further contains from 2 to
  10 % by weight of resin.
  - 8. Cold sealable barrier paper according to any of claims 1 to 7, characterized in that the mixture of acrylic polymers represents 100 % by dry weight of the layer.
  - 9. Cold sealable barrier paper according to claim 2, **characterized** in that the ethylene/vinyl alcohol (EVOH) copolymer or the polyvinyl alcohol (PVA) represents 100 % by dry weight of the layer.
- 30 10. Heat sealable barrier paper consisting of an actual support paper (1) printed or printable on the face side thereof, characterized in that it consists, at least on its reverse side, of a heat sealable layer and water vapour barrier layer

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(4), said water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65.

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- 11. Heat sealable barrier paper consisting of an actual support paper (1) printed or printable on the face side thereof, **characterized** in that it consists, at least on its reverse side, of a heat sealable layer and water vapour barrier layer (4), the water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, and of an oxygen aroma barrier layer (5) between the actual paper (1) and the water vapour barrier layer (4), the oxygen aroma barrier layer (5) consisting of ethylene/vinyl alcohol (EVOH) copolymer and polyvinyl alcohol (PVA) polymer, the mass of which is between 3 and 4 g/m<sup>2</sup>.
- 12. Heat sealable barrier paper consisting of an actual support paper (1) printed or printable on the face side thereof, **characterized** in that it consists, at least on its reverse side, of a heat sealable layer and water vapour barrier layer (4), the water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, and of an oxygen aroma barrier layer (5) between the actual paper (1) and the water vapour barrier layer (4), the oxygen aroma barrier layer (5) consisting of ethylene/vinyl alcohol (EVOH) copolymer and polyvinyl alcohol (PVA) polymer as a mixture with other polymers or as a mixture with mineral fillers, the EVOH or PVA representing at least 50 % by weight of the layer.
- 13. Heat sealable barrier paper according to any of claims 10 to 12,
  characterized in that said heat sealable layer and water vapour barrier layer is a unitary layer having both heat sealable and water vapour barrier properties.

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- 14. Heat sealable barrier paper according to any of claims 10 to 12, characterized in that it further contains a second water vapour barrier layer deposited directly on the printing.
- 5 15. Heat sealable barrier paper according to any of claims 10 to 14, characterized in that the mixture of acrylic polymers as an emulsion is a mixture of styrene acrylic polymers.
- 16. Heat sealable barrier paper according to any of claims 10 to 15, characterized in that the mixture of acrylic polymers further contains from 2 to 10 % by weight of resin.
  - 17. Heat sealable barrier paper according to any of claims 10 to 12, characterized in that the mixture of acrylic polymers represents 100% by dry weight of the layer.
  - 18. Heat sealable barrier paper according to claim 11, **characterized** in that the ethylene/vinyl alcohol (EVOH) copolymer or polyvinyl alcohol (PVA) represents 100 % by dry weight of the layer.
  - 19. Confectionery barrier paper consisting of an actual twistable support paper (1) printed on the face side thereof, **characterized** in that it further consists, directly in contact with the printing (2), of a water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65.
  - 20. Confectionery barrier paper consisting of an actual twistable support paper (1) printed on the face side thereof, **characterized** in that it further consists of a water vapour barrier layer (4) consisting of a mixture o of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and

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65, and of at least one oxygen and aroma barrier layer (5) consisting of an ethylene/vinyl alcohol (EVOH) copolymer or a polyvinyl alcohol (PVA) polymer, the mass of which is between 3 and 4 g/m<sup>2</sup>, positioned between the water vapour barrier layer (4) and the printing (2).

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- 21. Confectionery barrier paper consisting of an actual twistable support paper (1) printed on the face side thereof, characterized in that it further consists of a water vapour barrier layer (4) consisting of a mixture o of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, and of at least one oxygen and aroma barrier layer (5) consisting of an ethylene/vinyl alcohol (EVOH) copolymer or a polyvinyl alcohol (PVA) polymer as a mixture with other polymers or as a mixture with mineral fillers, the EVOH or PVA representing at least 50 % by weight of the layer, the mass of which is between 3 and 4 g/m², positioned between the water vapour barrier layer (4) and the printing (2).
- 22. Confectionery barrier paper consisting of an actual twistable support paper printed on the face side thereof, **characterized** in that it further consists, directly in contact with the printing (2), of a water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, and of a paraffin layer (7) having a mass of 2-6 g/m<sup>2</sup> on the reverse side of the support paper (1).

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23. Confectionery barrier paper consisting of an actual twistable support paper printed on the face side thereof, **characterized** in that it further consists of a water vapour barrier layer (4) consisting of a mixture of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, of at least one oxygen and aroma barrier layer (5) consisting of an ethylene/vinyl alcohol (EVOH) copolymer or a polyvinyl alcohol (PVA) polymer, the mass of which is

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between 3 and 4 g/m<sup>2</sup>, positioned between the water vapour barrier layer (4) and the printing (2), and of a paraffin layer (7) having a mass of 2 - 6 g/m<sup>2</sup> on the reverse side of the support paper (1).

- Confectionery barrier paper consisting of an actual twistable support 24. 5 paper (1) printed on the face side thereof, characterized in that it further consists of a water vapour barrier layer (4) consisting of a mixture o of acrylic polymers, and less than 5% of wax by weight, which has been applied as an emulsion, the total acid number of the acrylic polymers being between 30 and 65, of at least one oxygen and aroma barrier layer (5) consisting of an 10 ethylene/vinyl alcohol (EVOH) copolymer or a polyvinyl alcohol (PVA) polymer as a mixture with other polymers or as a mixture with mineral fillers, the EVOH or PVA representing at least 50 % by weight of the layer, the mass of which is between 3 and 4 g/m<sup>2</sup>, positioned between the water vapour barrier layer (4) and 15 the printing (2), and of a paraffin layer (7) having a mass of 2 - 6 g/m2 on the reverse side of the support paper (1).
  - 25. Confectionery paper according to any of claims 19 to 24, characterized in that the mixture of acrylic polymers as an emulsion is a mixture of styrene acrylic polymers.
  - 26. Confectionery paper according to any of claims 19 to 24, characterized in that the mixture of acrylic polymers further contains from 2 to 10 % by weight of resin.
  - 27. Confectionery paper according to any of claims 19 to 24, characterized in that the mixture of acrylic polymers represents 100 % by dry weight of the layer.
- 28. Confectionery paper according to any of claims 20 or 23, characterized in that the ethylene/vinyl alcohol (EVOH) copolymer or polyvinyl alcohol (PVA) represents 100 % by dry weight of the layer.